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SOURCES OF PULSED RADIATION¹

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ABSTRACT

Characteristics of various sources of pulsed radiation are examined from the viewpoint of their importance to the radiation chemist, and some examples of uses of such sources are mentioned. A summary is given of the application of methods of physical dosimetry to pulsed sources, and the calibration of convenient chemical dosimeters by physical dosimetry is outlined.

1. INTRODUCTION

An attempt will be made here to describe the ways in which a variety of pulsed sources have been used. The characteristics of typical sources will be discussed from the viewpoint of parameters important to the experimentalist. As will be seen, several different sources have been used with success in studying radiation induced reactions despite orders of magnitude differences in parameters such as beam current, pulse length, and dose per pulse. A low dose per pulse is sufficient if detection methods of high sensitivity can be used.

The time scale of the process being studied has an important bearing on the requirements for the pulsed source. It is clear that the advantages of the pulsed method would be diminished if measurements were possible only during the pulse because of short transient lifetime relative to the pulse length. Sometimes the experimental conditions can be arranged such that the lifetimes of species are lengthened, in which case the use of a source which is limited to long pulse lengths is no disadvantage. However, for

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second-order transient decay, obtaining longer lifetimes requires that lower transient concentrations be used, and the limit of detection sensitivity therefore becomes important. Problems of reaction of transient species with impurities or with the solvent can arise if low transient concentrations are used to slow down second-order reactions. In general, the shorter the radiation pulse available, the more flexible are the experimental requirements.

Types of pulsed sources which have been used will be discussed in the following with examples of experiments being given to point out areas where a particular pulsed source may be especially useful. Published material used in preparing this summary includes references 1-5.

2. TYPES OF PULSED RADIATION SOURCES

In Table I a list is presented of pulsed sources which have been used, and approximate values of relevant parameters of these sources. A parameter of prime importance is the dose per pulse, which is seen to vary over many orders of magnitude. Values are given for typical conditions such as distance from the beam exit window and degree of beam focusing.

Table I. Examples of Types of Pulsed Radiation Sources

Type	Particle	Energy (MeV)	Pulse Length (ns)	Peak Amps	Dose per Pulse (krad)	Repetition Rate (s^{-1})
Linac (L-band)	e^{-}	20	0.03	200	2	800
			10	20	60	100
			3000	2	2000	30
Febetron 705	e^{-}	1.8	50	5000	2000	0.01
Febetron 706	e^{-}	0.5	4	7000	800	0.01
Van de Graaff	e^{-}	3	1	5	1	10^5
			100	5	100	10^5
Van de Graaff	H^{+}	2	0.2	10^{-5}	10^{-4}	10^6
Tandem Van de Graaff	H^{+}	9	1	10^{-4}	10^{-3}	10^6
Cyclotron	H^{+}	10	10^4	10^{-6}	0.05	10^3
X-ray unit	-	0.12	10^6	-	10^{-4}	10

The energy of an electron beam is important mainly in two respects. If the energy is much below 0.5 MeV, difficulties arise with respect to absorption and scattering in windows and in the inconveniently small penetration depths in the case of condensed phase samples. From the standpoint of radiation chemistry, there is no use in beams of more than about 20 MeV, and at energies above this induced radioactivity can become a problem.

The repetition rate is an important parameter because many experiments are possible only with the use of signal averaging techniques. Such techniques are now widely used in current pulse-radiolysis work due to developments in signal averaging devices and especially to the general computerization of experiments. Extensive signal averaging is practical with most of the sources given in Table I. The Febetrons can only be pulsed about once a minute, so only a limited amount of signal averaging is practical; however, the large pulse from a Febetron often obviates the necessity of signal averaging.

2.1. Microwave Linear Accelerators

Details concerning operating versions of "L-band" and "S-band" accelerators are available in the literature (6-8) and will not be given here. A characteristic of these machines is that without "prebunching", i.e., a technique by which several fine-structure pulses are combined to form one pulse (7), the pulses produced (duration ~ 5 ns to ~ 10 μ s) actually consist of a series of fine-structure pulses of width on the order of 20-30 picoseconds. Figure 1 shows part of such a series for an "S-band" machine. In the case of the "S-band" machine the spacing between pulses is 350 ps while the "L-band" machine gives 770 ps spacing. The "L-band"

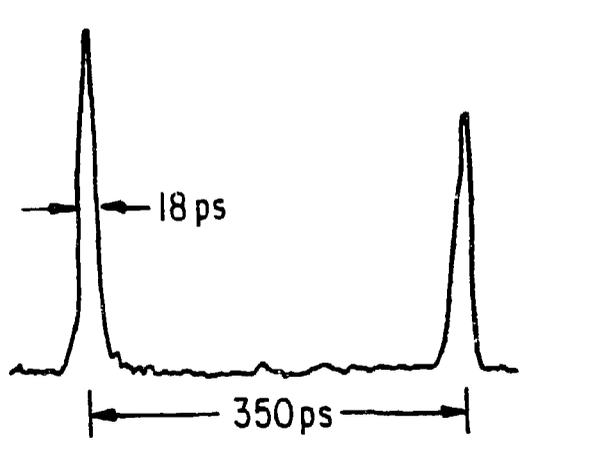


Figure 1. Streak camera record of S-band linac fine structure pulses (8), using Cerenkov light.

machines have the advantage of considerably higher currents, while the "S-band" machines have somewhat narrower fine-structure pulses.

In using such chains of fine-structure pulses in pulse-radiolysis experiments, one must bear in mind the possibility of intensity effects due to the pulse structure. The approximation that the pulse is "uniform" can only be made if the lifetime of transient species of importance in the chemical reactions being considered is long compared with the fine-structure spacing.

To gain a better understanding of radiation induced transient species and their reactions, it is often desirable to examine processes occurring at as early a time as possible. The 20-30 ps fine-structure pulses afford the opportunity to attain time resolution on the order of 20 ps, and experiments of this type were first done (9) with water where the hydrated electron was measured in the time between fine structure pulses. The development of the "subharmonic prebunching" technique (7) to produce single 30 ps pulses (singly or separated by milliseconds) as shown in Figure 2, removed the limitation of having a second pulse occur after 770 ps.

Detection methods are a determining factor in the utilization of the 30 ps pulse. In 1970, rise-times of optical detection (photomultipliers, photodiodes) were not better than about 100 ps. Therefore, methods were devised (9,11,12), which will be discussed elsewhere in this volume, for producing 30 ps pulses of Cerenkov light (using part of the electron pulse), and measuring the absorbance in liquid samples using this Cerenkov light, which was delayed a time t (variable) with respect to the electron pulse. The time resolution is therefore essentially determined by the electron

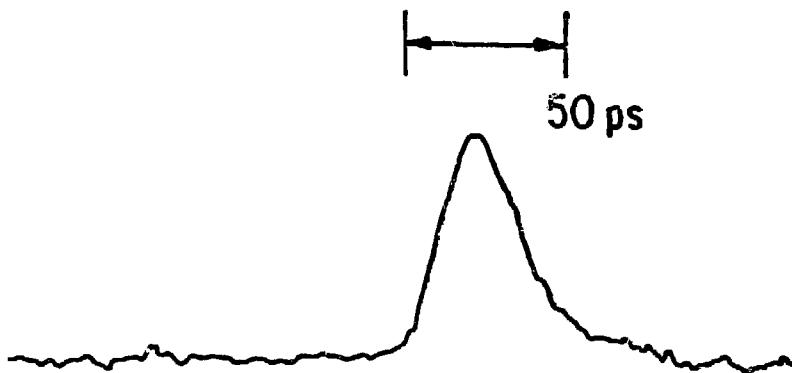


Figure 2. Single pulse after subharmonic prebunching; measured by streak camera recording of Cerenkov light (10).

pulse width, because the Cerenkov light has the same width as the electron pulse.

More recently, pulses of 30 picosecond duration have been used to investigate fluorescence from gas and liquid samples, using a photodiode or crossed-field photomultiplier to obtain time resolution of about 100 ps (13). Improvement on this time resolution has been attained by the use of streak camera techniques (14) for recording fluorescence from hydrocarbon solutions of organic scintillators, where time resolution approaching the pulse width has been obtained. The use of streak camera techniques in the picosecond time regime has been primarily in studies of light emission because of problems caused by the high light intensities needed for good signal-to-noise ratio in optical absorption measurements made in the picosecond regime.

Linear accelerators with or without the capability of single psec pulses can be used under conditions where the pulse is many microseconds long. This capability allows doses per pulse to be obtained comparable to doses obtained from Febetrons (see Table I). For gas phase work, this is convenient in the following way. Most gas phase studies of atomic and free radical reactions do not require time resolution better than several microseconds, because of the fact that radical-radical recombination times are in the range of hundreds of microseconds for transient concentrations which are typically attainable. Therefore, the linear accelerator can be used, for example, for studies where it is desired to put the electron beam through the wall of a high-temperature (ca. 1000°C) oven (15). The 15-20 MeV energy of the electrons is convenient in this respect, when compared with the (maximum) 2 MeV electrons from a Febetron, which create an undesirable situation when a high temperature cell is used. That is, if the windows are made thin enough to allow the 2 MeV beam to pass through, too much heat loss to the Febetron occurs; therefore, a temperature limit of about 200°C exists for Febetron work. The lower concentration of species produced by the "weaker" linac pulse, and the smaller useable irradiated volume can be compensated for by making use of the greater pulse repetition rate available and using signal averaging techniques.

2.2. Febetrons

Febetrons, the trade-name for pulsed sources produced originally by the Field Emission Corporation, operate on field emission principle, using a Marx surge circuit to supply a large DC voltage pulse which causes electrons to be emitted from the cathode and accelerated to the anode. These machines produce single pulses of electrons at a maximum rate of about one per minute. The pulse produced is quite different from a typical linac pulse; it does not consist of a chain of fine structure pulses and is orders of

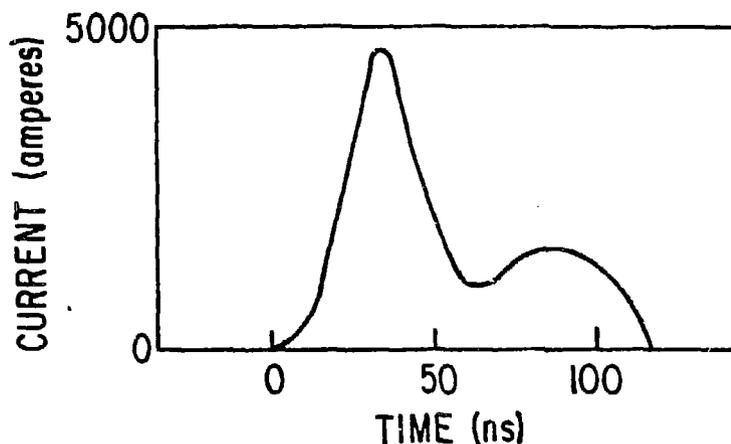


Figure 3. Current waveform of electron pulse from Febetron 705 measured with a Faraday cup (16).

magnitude higher in current and lower in energy (see Table I). The lower energy and high current make the Febetron more suitable for gas phase work, although there have been significant applications to condensed phases. The small penetration depth in condensed phases leads to concentrations of transients which are usually unnecessarily high.

The pulse shape from a Febetron 705 is shown in Figure 3. Because of the fact that the use of shorter pulses from the Febetron 706 or linear accelerator allows time resolution in the nsec region, studies involving the 705 have been mainly of processes occurring on time scales of many microseconds.

Figure 4 shows an application to the reaction of HO_2 with NO , producing NO_2 which is observed at 404.7 nm (17). The absorbance, $A_{404.7}$, is rather weak and requires a blank correction to be made in order to correct for absorbance in the cell window and a reproducible "noise" pattern on the analyzing light (see Figure 4).

A problem which often arises, particularly with the Febetrons, is the creation of "noise" due to the electromagnetic fields produced coincident with the very high current, short duration electron pulse. The fields cause disturbances in the electronics used to measure changes in absorbed or emitted light. The use of double copper screened rooms, in which the fast detection and amplification equipment is placed, has been found to reduce the interference to tolerable levels.

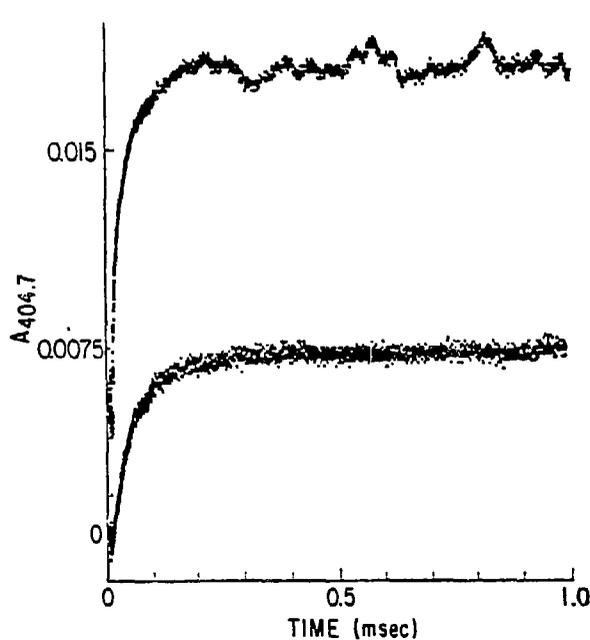


Figure 4. Example of use of Febetron 705 to observe NO_2 production in the reaction of H_2O_2 with NO (1190 torr H_2 , 2.5 torr O_2 , 0.13 torr NO). The lower curve results from subtracting the "blank" (not shown) on 1200 torr H_2 alone from the upper curve (which has been shifted vertically for convenience in presentation).

2.3. Other Sources of Pulsed Radiation

Van de Graaff generators have been used successfully to produce nanosecond (and shorter) pulses of electrons with peak current of about 5 amps (18). The Van de Graaff accelerator normally produces a continuous beam (with no fine-structure pulses) but is modified to produce pulses by controlling the voltage on the grid of the electron gun. Pulses of length between 1 and 100 ns can readily be obtained, maintaining up to about 5 amp current during the pulse. Thus, the dose per pulse is comparable to that from a linac for an equivalent pulse length. A disadvantage is that the beam divergence is greater due to the lower electron energy (3 MeV) typical of Van de Graaff sources.

A pulsed Van de Graaff source has also been used recently (19) to study the yield of the hydrated electron in water at nanosecond times using a 1 ns beam of 3 MeV protons. Because the penetration depth for 3 MeV protons is only about 0.15 mm, an ingenious method of putting a laser beam along the axis of a narrow jet of water was used to measure the optical absorbance due to the hydrated electron.

CYCLOTRON PULSE-RADIOLYSIS

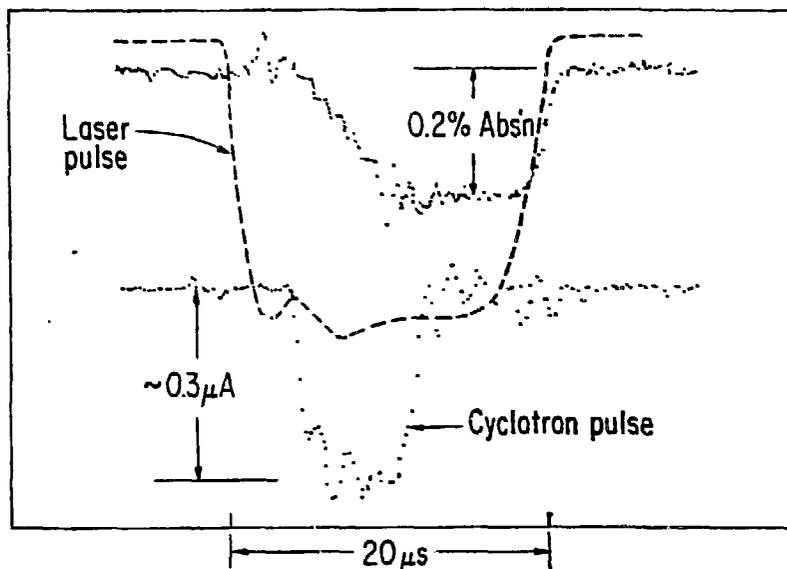


Figure 5. An example of the use of an $8 \mu\text{s}$ beam of 20 MeV deuterons from a cyclotron (21). The absorption of $(\text{CNS})_2$ at 514.5 nm is measured in an aqueous KCNS solution with an argon ion laser.

In comparison with pulsed-electron radiolysis, few studies have been made in condensed phases using pulses of protons or heavier ions. This is partially due to the problem just mentioned of small penetration depth. High energy particles with greater penetration depth can be produced by other means, but in general currents are low and/or pulse lengths less than microseconds are not available. In the past several years, G-values of primary species in water have been studied at microsecond times using 10 microsecond pulses of deuterons and helium ions from a cyclotron (20) (see Figure 5). Information is obtained on the effect of LET (linear energy transfer, i.e., the amount of energy transferred per unit distance along the track of the particle) and particle type on G-values, which is used to improve the theories of diffusion kinetics and track structure which are used to model such results.

Proton and helium ion beams of nanosecond length from Van de Graaff accelerators have also been used in recent years to investigate LET effects by observing the time dependence of fluorescence from benzene in cyclohexane (22). However, there is a need for more work at nanosecond times in this area of high LET radiation chemistry, to determine whether time dependences of transient G-values follow the predictions of models being used. The results

in Figure 5 indicate how a rather weak absorption can be measured by appropriate signal averaging; hopefully, the effects of a variety of high LET particles will be investigated using such techniques with nanosecond pulses in the future.

Pulses of 2 MeV protons of 15 nsec duration from a Van de Graaff have been used to study processes occurring in rare gases by means of examining the time dependences of optical emissions from the vacuum uv through the visible region (23). The small penetration depth is not a problem in the gas phase; in fact, the higher LET is an advantage.

Pulses of low intensity x-rays (see Table I) have also been used in a series of experiments on ion-recombination in the gas phase (24). The reason that a dose per pulse at least five orders of magnitude lower than is typical of electron pulses can be used is that very sensitive techniques exist for measuring charge.

3. PHYSICAL DOSIMETRY FOR PULSED SOURCES

For most practical purposes, in the case of an experimental set-up where optical absorptions are being measured, there is no need for physical dosimetry, i.e., calorimetric methods, or ionization chamber methods. The reason for this is that considerable effort has been devoted to the problem of accurate physical dosimetry, and the G-values of products in various chemical dosimeters have been determined on the basis of this physical dosimetry (3-5). Thus, for both gas and condensed phase irradiations, convenient chemical systems can be routinely used, by optically monitoring product formation after a pulse, to accurately establish the dose under the same geometrical conditions to be used for other samples. Even in the case where optical absorption is not used as a measuring technique, the dose can be established by measuring chemical products (e.g., N_2 from N_2O) from established chemical dosimeters.

Because of the localized and directional nature of a pulsed source, consideration has to be given to the effect of beam scattering on the dose deposited. For an electron beam entering a liquid sample, the axial dose will decrease with depth if the initial beam diameter is much smaller than the range, due to scattering. But, if broad beam geometry is used, the axial dose actually increases significantly with depth before decreasing (1). In the case of gas samples, the scattering of the beam is more significant; a 13 MeV beam passing through 1.5 mm quartz windows was found to scatter enough that the dose decreased a factor of two in about 3 cm (25). The point to be made is that beam scattering must be kept in mind in order that the dosimetry is appropriate for a particular experimental situation.

For high dose pulsed sources, calorimetry has been the primary method used for absolute dosimetry (2). Ionization chamber methods can also be applied to pulsed sources (26); the charge produced by a pulse is measured and can be related to the dose if the energy required to produce an ion pair is known for the gas in the ionization chamber. However, for high intensity pulses the use of ion chambers requires corrections to relate the observed currents to dose, and has not been a frequently applied method (26).

In the case of water, a pulse of 10^5 rads will produce enough of a temperature rise (2.4°C) to be readily measured. The general procedure is to use a thermocouple to measure the temperature rise. Correction must be made for the small amount ($\sim 5\%$) of energy which produces chemical change rather than heat. If the pulse is short and thermocouple wires of diameter less than about 0.07 mm (4) are used in water, the system is essentially adiabatic, i.e., heat loss corrections are not appreciable during the fraction of a second needed for the thermocouple to reach equilibrium with the water. An example of a calorimetric measurement of dose used in calibrating the Fricke dosimeter at high dose rates from a linear accelerator is given by the work of Anderson (27). A recent publication by Pañta (28) describes a calorimetric method for measurement of single linac pulses of 100 rads to 130 krad, similar in response characteristics to the method described below, and gives a thorough discussion of the theoretical principles involved in such measurements.

The dose from a pulse can be measured by directly irradiating a thermocouple (or several thermocouples in series). This method has been used by Willis and co-workers (16,29,30) for conditions applicable to both gas and liquid phase irradiations using the high intensity pulses from Febetrons. For the liquid phase, using a Febetron 705, a thin disc (graphite, aluminum, or nickel) was used, with thickness being varied such that all or part of the beam was absorbed. The response from a thermocouple attached to an aluminum disc appeared qualitatively as shown in Figure 6. The response time of the recorder is responsible for the initial rise, and the sharp peak at the beginning is due partly to the lower specific heat of the thermocouple compared with that of aluminum, but primarily to the fact that the thermocouple was at the center of the disc, where the radiation intensity was higher, and hence, the temperature change was initially greater. The negative peak is an artifact due to the switching off of the focussing magnet on the Febetron 705 about 2 sec after the pulse. The subsequent cooling curve is extrapolated back to time zero, and that reading of the thermocouple is converted to a temperature rise. The dose is then determined from the known specific heat of aluminum.

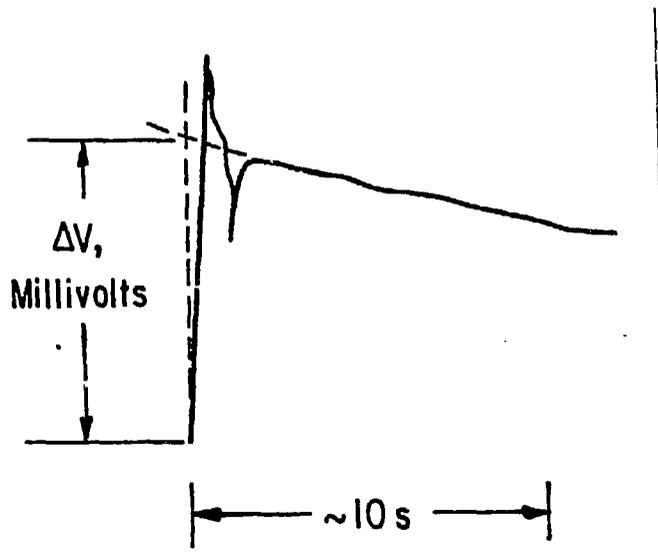


Figure 6. Thermocouple output from an aluminum calorimeter (16) following a 100 ns electron pulse from a Febetron 705.

From data obtained as a function of the thickness of the calorimeter material, the dose to a liquid sample put in the same position was calculated.

For gas samples, irradiated with either the Febetron 705 or 706, similar measurements were made using aluminum calorimeters, yielding curves similar to that shown in Figure 6. In the case of the Febetron 705, measurements were made at several positions near the Febetron window over a range of about 3 cm. The mean dose measured over this range as a function of calorimeter thickness is shown in Figure 7. Extrapolation to zero thickness allows the mean dose to a sample gas in the cell to be obtained.

Using the dose determined in this way, the $G(N_2)$ from N_2O was determined to be 12.4 ± 0.2 molecules per 100 eV for the Febetron 705 (16) (~ 100 ns pulse, 2.3 Mrad). In the case of the Febetron 706, the same calorimetric method was applied (30), and $G(N_2)$ from N_2O was determined to be 12.3 ± 0.3 molecules per 100 eV (~ 5 ns pulse, 0.9 Mrad). This chemical dosimeter can, of course, be used by the experimenter instead of calorimetric procedures. However, it should be noted that when an optical absorption experiment is being carried out and the dose in the path traversed by the optical beam is desired, it is much more convenient to measure the concentration of O_3 formed in an atmosphere of O_2 containing $\sim 0.5\%$ SF_6 . This system has been determined to have $G(O_3) = 6.2$ (31,32). The known absorption coefficient of ozone can be used to determine its concentration after its formation is complete (a

few msec after a pulse), and hence the dose to that part of the sample in the optical path can be determined. This is convenient for measuring G-values of other optically absorbing transient species, assuming their absorption coefficients are known.

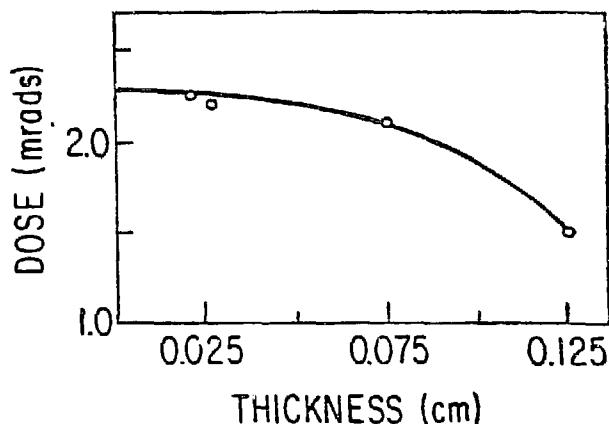


Figure 7. Mean dose for a gas cell, using a 100 ns pulse from a Febetron 705, as a function of calorimeter thickness (16).

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